Overview of Capacitive Deionization

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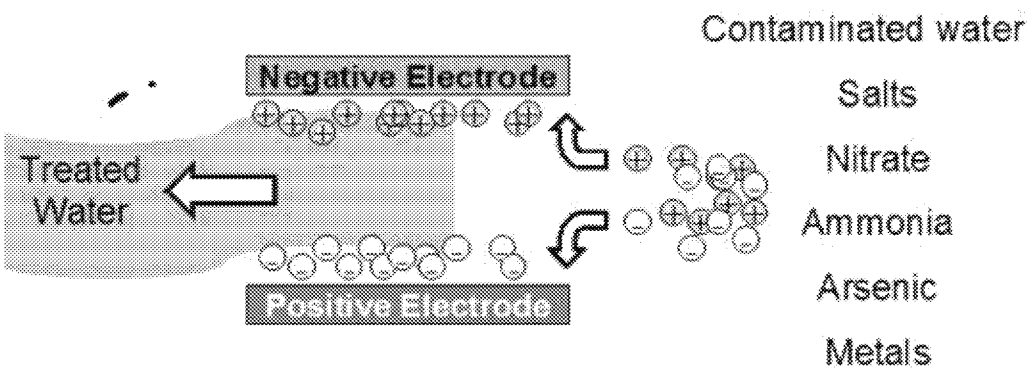


Capacitive Deionization (also known as Flow Through Capacitor) is one of the only alternatives to the commonly used technology of reverse osmosis, and among the few methods ever invented applicable to total dissolved solids (t.d.s), such as salts, sulfate nitrate, fluoride, heavy metals, minerals, and other dissolved ions. T.d.s is the most difficult to treat and often the rate limiting contaminant in water purification. The deceptively simple idea of capacitive deionization uses high surface electrodes to remove contaminants by capacitive charging. Upon application of a small voltage of one or two volts to the electrodes, a batch of purified water is generated. When the capacitor is electronically shunted or reversed, a smaller batch of concentrated waste is released, thereby readying the cell for the next charge-purification cycle. The major operating difference between capacitive deionization and reverse osmosis is that no sustained concentrate is formed. It is this concentrate that causes fouling, solidification of minerals onto reverse osmosis membranes, excessive waste water, energy, and operating costs. Averaged over time in a capacitive deionization flow cell however, there is also no change in concentration. Moreover, bacteria that tend to foul surfaces of membranes also do not like the rapidly changing concentrations, along with steep voltage gradients on the order of one billion volts per meter. As a result, this system is more robust at higher water recoveries than reverse osmosis.[i]

Historical Development Of Capacitive Deionization Into a Useful Technology

Work on Capacitive Deionization began in the early sixties. The first explicit recognition that capacitance may be used as the operating principal in water purification was by James Benak[ii], with Standard oil, in 1966. Other work in this period by various researchers at US Bureau of Saline water[iii] also used electrodes to desalinate water. These early designs used thick, resistive beds of carbon and poorly connected current collectors, and it is uncertain if the actual mechanism was capacitive charging or electrolysis. The entire field died out completely in the early 1970s, until Marc Andelman's work on Flow Through Capacitors in the early 1990s', and, work using aerogel electrodes by the University of California a little later. These designs used improved capacitor engineering of thin electrodes and better contacts. However, all of these early designs did not work. The reason was inefficiency caused by the pore volume in capacitor electrodes. This pore volume is necessary to provide the surface area for good capacitance. However, this pore volume causes the electrode to hold salts inside the electrode like a sponge, so that the electrode cannot efficiently be rinsed out. These salts therefore contaminate the purified water. Andelman solved this problem by using fuel cell like- ion exchange membranes that hold the pore volume salt inside the electrode[iv] .This is what finally allowed the technology to be practiced commercially. This so-called membrane capacitive deionization is actually a hybrid between electrodialysis and true capacitive deionization. Like capacitive deionization, the electric current is driven by capacitive deionization and not Faradaic (as in electrolysis and breaking chemical bonds) reactions. However, like electrodialysis, there still exists a concentrated solution, in this case, on the electrode side of a membrane. Capacitive deionization is now a field with dedicated seminars and many hundreds of publications. Academics rarely cite the patent literature where this field started and continues to develop, and misconceptions abound in this field. The application critical need to correct for pore volume ions is not always recognized even today.

Applications of Capacitive Deoinization

Cooling Towers[v]

Agriculture[vi]

Point of Use and coffee shops.[vii]

Salt-less water softener for Point of Entry Residential Use

Industrial[viii]

Commercial Laundry[ix]

Appliances[x]

Carbon Capture[xi]

Companies in Capacitive Deionization

Membrane capacitive deionization is well on the market due to its energy, water recovery, and operation advantages for various total dissolved solids, hard and brackish waters.[xii] Various small businesses have led the way to commercialize capacitive deionization. Most companies selling a workable product use the membrane version of capacitive deionization, and most have had some connection at some time with Marc Andelman, either using or infringing his patents. A partial list is as follows.

Voltea B.V. Sassenheim The Netherlands, www.Voltea.com. This company formed by the acquisition of Marc Andelman's earlier set of patents by Unilever. This is the only company operating legally under Andelman's over thirty issued previous patents.

Various other small companies promote capacitive deionization, often for poorly developed products, or, products that do not exist. Most of these are former terminated, licensees of Andelman, or companies worldwide that picked this up from Andelman's terminated licensees. There are also some Korean and Chinese companies. A partial list as follows.

Idropan Milan, Italy http://www.idropan.com/en/ .

Estpure, China. Claims to have plants in the 10,000 metric ton per day range[xiii].

Siontech Korea http://www.siontech.co.kr/.

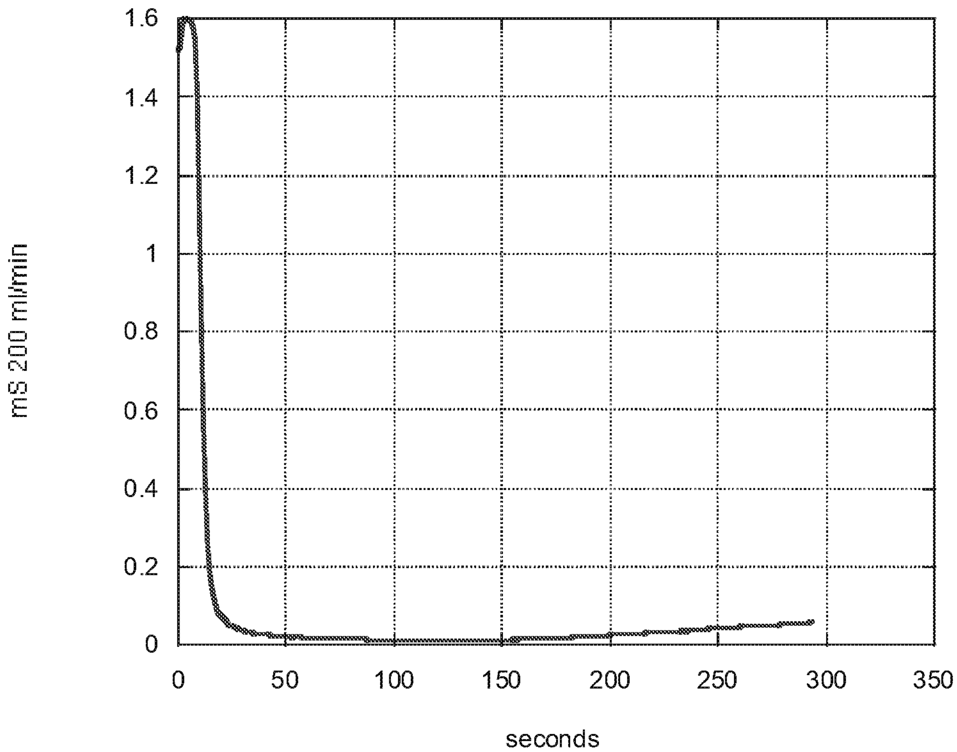
The only companies that have consistently sold products are Voltea and Idropan. There are also a number of garage scale, small companies in India trying to build products. Pilots have been placed in Bangladesh by Idropan and Voltea. Voltea's former partner Pentair once had a size-able effort that included field trials, in order to introduce capacitive deionization as a residential water softener[xiv]. This was cancelled, likely due to the cost of the product.

Mespilus inc. This is Marc Andelman's company. He operates a virtual business. Marc recently activated a group of people with 100 years of combined experience to deliver upon a pilot contract to a multinational with a consumer products application.

An Important New Development, True Capacitive Deionization.

- **Third generation, membrane-less capacitive deionization**[xv]. Paten allowed or issued as of 2018 the USA, China, Australia, pending elsewhere. This works without the most expensive, bulky and problematic part of the earlier technology, the fuel cell-like ion exchange membranes. These membranes are a major cost in the earlier flow cell. This makes a failure of the working flow cell component like changing golden tires on a car, adding operating cost and risk. The membranes also leak water and salt, lowering energy efficiency and limiting use to feed water under 3000 ppm. A recent development, also by Andelman, represents true capacitive deionization without the fuel cell-like ion exchange membranes. As per the above referenced material, this works by functionalizing the electrode pore surfaces in such a way as to repel and prevent the problem causing pore ions. This represents a major improvement, because, for the first time, an alternative desalination and t.d.s method exists where the working flow cell part is entirely made from cheap materials. The electrode may be made from activated carbon, already used in water and one of the world's highest volume commodities. It is possible that this development will also extend the use of capacitive deionization to higher concentrations. Finally, because of the known relationship between through put and energy in capacitive deionization, it is possible to use a larger cell size for a given flow at less energy usage. The less expensive third generation flow cell makes this possible due to affordability of a larger cell. Patents very recently issued or allowed in the USA, China, and, Australia, pending elsewhere

State of Development.
The below results were obtained by a large company in Europe that recently purchased a pilot. These results used 1 mS hard water (about 500 ppm). This technology is achieving close to 99% purification at decent flow rates per amount of electrode. The earlier, membrane version cannot do this. If there is no need for such extreme purification, flow rate may be faster and therefore cheaper. Third Generation CDI will be able to treat at least up to 5000 ppm, and, may in theory extend the range of CDI to seawater.



Other Future Directions

- Application of capacitive Deionization has extended to CO2 capture[xvi]. This is at an early stage of development.

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[i] Webinar by an engineering firm on application of membrane capacitive deionization here: https://www.youtube.com/watch?v=Hn7L5JA8AXQ

[ii] US3658674A Process for demineralization of water, 1966

[iii] 3Office of Saline Water Research and Development Progress Report No. 516, March 1970, U.S. Department of the Interior PB 200 056, entitled The Electrosorb Process for Desalting Water, by Allan M. Johnson et al., hereinafter referred to as the "Department of the Interior Report" and further in an article entitled "Desalting by Means of Porous Carbon Electrodes" by J. Newman et al., in J. Electrochem. Soc.: Electrochemical Technology, March 1971, Pages 510-517, hereinafter referred to as the "Newman Article", both of which are incorporated herein by reference. A comparable process is also described in NTIS research and development progress report No. OSW-

PR-188, by Danny D. Caudle et al., Electrochemical Demineralization of Water with Carbon Electrodes, May, 1966.
[iv] US6709560B2 Charge Barrie Flow Through Capacitor, Andelman priority 2004

[v] http://voltea.com/2017/02/06/voltea-releases-capdi-cooling-towers-case-study/
[vi] http://voltea.com/ag-tech-english/
[vii] http://voltea.com/2017/11/12/voltea-launches-first-capdi-point-use-product-diuse/
[viii] https://www.youtube.com/watch?v=2iBB6WF3B0c&t=39s,
https://www.youtube.com/watch?v=Ih3dWaExmRw&t=46s
[ix] http://voltea.com/2017/03/31/voltea-releases-capdi-commercial-laundry-case-study/
[x] http://voltea.com/consumer-appliances-english/
[xi] Capacitance for Carbon Capture, Kai Landskron, Angewandte Chemie 22 February 2018 https://doi.org/10.1002/anie.201800941
[xii] Webinar by an engineering firm on application of membrane capacitive deionization here; https://www.youtube.com/watch?v=Hn7L5JA8AXQ

[xiii]

https://web.archive.org/web/20131203014753/http://estpure.com/a/cases/detail_62.aspx

[xiv] https://www.prnewswire.com/news-releases/pentair-hybrid-di-water-conditioning-to-debut-in-us-141799523.html
[xv] : Andelman, M. (2014) Ionic Group Derivitized Nano Porous Carbon Electrodes for Capacitive Deionization. Journal of Materials Science and Chemical Engineering, 2, 16-22. http://dx.doi.org/10.4236/msce.2014.23002

[xvi] Capacitance for Carbon Capture, Kai Landskron, Angewandte Chemie 22 February 2018 https://doi.org/10.1002/anie.201800941